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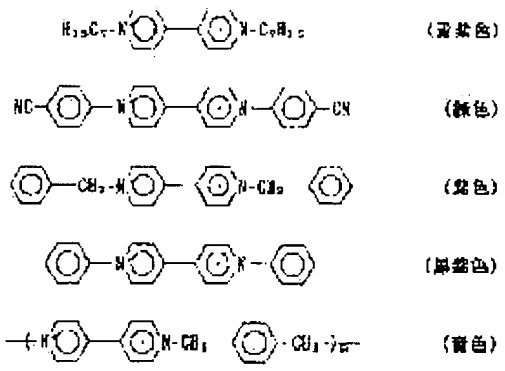
(54) ELECTROCHROMIC ELEMENT

(57)Abstract:

PURPOSE: To provide the electrochromic element which can make multicolor display by packing a soln. prepd. by dissolving a biologen deriv. into a polyethylene(PE) oxide electrolyte into the holes of a solid-state high-polymer porous thin film.

CONSTITUTION: The biologen deriv. is dissolved into the PE oxide electrolyte of about 100 to 1000 mol.wt. to prepare the soln. and this soln. is packed into the pores of the solid-state high-polymer porous thin film. Polyolefin, polytetrafluoroethylene, etc., are usable as the solid-state high-polymer porous thin film. The polyolefins having ≥5×105 weight mol.wt. are more preferable for the ease of designing a porous structure and compatibly attaining thinner films and higher mechanical strength. The biologen deriv. refers to 4,4'-bipyricline deriv. and is the oxidation reduction type compd., the oxidation type of which is colorless and the reduction type of which is blue to purple. Multiple colors are obtainable with the derivatives which are formed by methylation and benzylation of 4,4-bipyricline by selecting the kinds of the derivatives. The derivatives are exemplified by formula.



LEGAL STATUS

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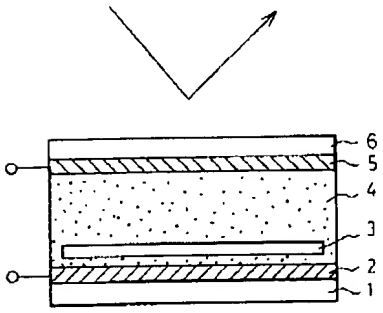
Drawing selection drawing 1



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CLAIMS

[Claim(s)]
[Claim 1] The electrochromic element characterized by using the electrolyte thin film which comes to fill up the solution which dissolved the viologen derivative in the polyethylene-oxide system electrolyte during hole of a solid-state macromolecule porosity thin film.

[Translation done.]

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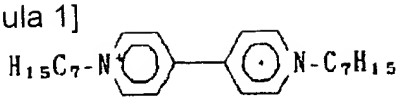
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] this invention relates to an electrochromic element.
[0002]
[Description of the Prior Art] The interest is increasing in the element adapting the electrochromic (EC) phenomenon in which the color of the matter changes with voltage in reversible. An electrochromic element (ECD) has the features, like there is memory nature in which a bright legible large area display is possible (there is little power consumption), and has modulated light elements, such as the large-sized plotting boards, such as a stock price display, a message board, and a guide plate, and an anti-dazzle mirror of an automobile, modulated light glass (aperture), and sunglasses, as application in which such a feature was harnessed.
[0003] The typical structure of ECD is WO3, when an electrolyte is arranged, it changes between an electrochromic electrode (WO3) and a counter electrode and voltage is impressed between two electrodes. By the electron from the ion and power supply from an electrolyte, cathodic reduction is carried out and it colors. By the way, although there is a problem of a liquid spill and there is no problem on which a solid electrolyte deals with a liquid on the other hand when a liquid enters into an element, although the liquid electrolyte is excellent in responsibility as an electrolyte since ion conductivity is large, there is a fault that responsibility is bad. Then, these people indicated previously ECD using the electrolyte thin film which comes to fill up an ionic conductor during hole of a solid-state macromolecule porosity thin film as a solid electrolyte with high ion conductivity (Japanese Patent Application No. No. 48490 [two to]).
[0004] Moreover, the viologen derivative was dissolved in the solid polymer electrolyte of a polyethylene oxide, and it was indicated that what sandwiched this between the working electrode and the counter electrode can be used as ECD.
[0005]
[Problem(s) to be Solved by the Invention] Since the macromolecule solid-state polyethylene oxide is used for ECD which dissolves a viologen derivative in this polyethylene-oxide solid polymer electrolyte, and grows into it, its film intensity is low, and it has a fault with difficult large-area-izing. Then, this invention aims at offering ECD which canceled such a fault.
[0006]
[Means for Solving the Problem] In order to solve the above-mentioned technical problem, according to this invention, the electrochromic element characterized by using the electrolyte thin film which comes to fill up the solution which dissolved the viologen derivative in the polyethylene-oxide system electrolyte during hole of a solid-state macromolecule porosity thin film is offered.
[0007] A viologen derivative is a derivative of a 4 and 4'-bipyridine, and it is the oxidation reduction type compound [colorlessness] in which an oxidation type is shown and which a reduction type shows blue - purple. Methylation, the benzyl-ized derivative, and the following compound are illustrated in a 4 and 4'-bipyridine. This viologen derivative has the advantage which can realize multiple color by choosing the kind of derivative.
[0008]

[Formula 1]



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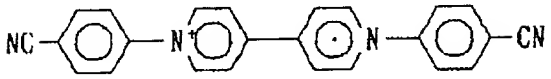

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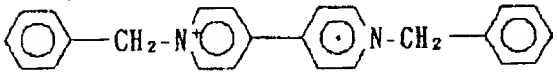

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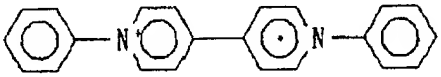

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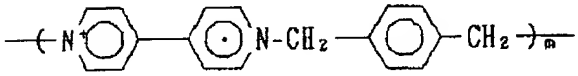

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[0009] This viologen derivative dissolves in a polyethylene-oxide system electrolyte. In this invention, a with a molecular weight of about 100 to 1000 polyethylene-oxide system electrolyte is used. If molecular weight is smaller than this, it will be hard to hold during hole of a thin film, and if larger than this, viscosity will be too large and ion conductivity will be reduced. In this way, what was obtained is filled up with ECD of this invention during hole of a solid-state macromolecule porosity thin film like JP,3-67227,A, and an electrolyte thin film is constituted. This electrolyte thin film holds the intensity of a solid-state macromolecule porosity thin film, and thin-film-izing and large-area-izing are possible for it.

[0010] For 0.1 micrometers - 50 micrometers and a void content, as a solid-state macromolecule porosity thin film of this invention, 40% - 90% and breaking strength are [thickness] 200 kg/cm2. That whose diameter of an average breakthrough is 0.01 micrometers - 0.7 micrometers is used preferably above. Generally the thickness of a thin film is 0.1 micrometers - 50 micrometers, and is 1.0 micrometers - 25 micrometers preferably. It is difficult for thickness to present practical use in less than 0.1 micrometers from the fall of the mechanical strength as a supporting lamella, and the field of handling nature. It is not desirable from a viewpoint of on the other hand stopping effective resistance low when exceeding 50 micrometers. It is 60% - 90% of range often [the void content of a porous thin film / considering as 40% - 90%], and preferably. When a void content becomes insufficient [less than 40% / the ion conductivity as an electrolyte] and exceeds 90% on the other hand, it is difficult for the mechanical strength as a supporting lamella to become small, and to present practical use.

[0011] Although the diameter of an average breakthrough just fixes an ionic conductor during hole, generally it is 0.01 micrometers - 0.7 micrometers. The desirable diameter of an average breakthrough is based also on the quality of the material of a poly membrane, or the configuration of a hole. Generally the breaking strength of a poly membrane is 200 kg/cm2. They are 500 kg/cm2 more preferably above. It is suitable for the utilization as a supporting lamella by having the above. The porous thin film used for this invention has a function as a base material of the above ionic conductors, and consists of polymeric materials which were excellent in the mechanical strength.

[0012] Although a polyolefine, a polytetrafluoroethylene, and a polyvinylidene fluoride can be used from a viewpoint of chemical stability, for example, especially for one example of suitable polymeric materials, weight average molecular weight is 5x105 from a viewpoint of the ease of coexistence of the design, thin-film-izing, and the mechanical strength of the porous structure of this invention. It is the above polyolefine. namely, the crystalline line of the homopolymer of an olefin, or a copolymer -- a polyolefine -- the weight average molecular weight -- 5x105 the above -- desirable -- 1x106 to 1x107 It is a thing. For example, polyethylene, polypropylene, an ethylene propylene rubber, polybdenum -1, the poly 4-methyl pentene -1, etc. are raised. Among these, weight average molecular weight is 5x105. The above polyethylene or polypropylene is desirable. The weight average molecular weight

of a polyolefine influences the mechanical strength of the transparency film obtained. By super-drawing, the amount polyolefine of super-macromolecules is ultra-thin, enables film production of high intensity, and is taken as the base material of the low quantity ion conductivity thin film of effective resistance. Weight average molecular weight is 5x105. Although the polyolefine of the following can be used simultaneously, weight average molecular weight is 5x105. By the system which does not contain the above polyolefine, the film of the ultra-thin high intensity by super-drawing is not obtained.

[0013] The above porous thin films can be manufactured by the following methods. Into a solvent like a liquid paraffin, the heating dissolution of 1 % of the weight - the 15 % of the weight is carried out, and let the amount polyolefine of super-macromolecules be a uniform solution. A sheet is formed from this solution, and it quenches and considers as a gel sheet. Extraction processing is carried out with a volatile solvent like a methylene chloride, and the amount of solvents contained in this gel sheet is made into 10 % of the weight - 90 % of the weight. This gel sheet is heated at the temperature below the melting point of a polyolefine, and it extends to 10 or more times for a field scale factor. The solvent contained in this extension film is dried after carrying out extraction removal with a volatile solvent like a methylene chloride.

[0014] The example of another suitable polymeric materials is a polycarbonate, and the solid-state macromolecule porosity thin film in this case irradiates a charged particle all over a reactor to a polycarbonate thin film, and can also be produced by the method of carrying out alkali etching of the track which the charged particle passed, and forming a hole. As for such a thin film, Kamiichi of a polycarbonate and the polyester product is carried out as for example, a new chestnut pore membrane.

[0015] In addition, polyester, poly methacrylate, a polyacetal, a polyvinylidene chloride, tetrafluoro polyethylene, etc. can be used. As a method filled up with an ionic conductor into a macromolecule thin film ** The viologen derivative dissolved in the solvent, or the viologen derivative made [the shape of a sol and the gel] to carry out differential powder into a solvent [whether a solid-state macromolecule porosity thin film is infiltrated and] By the manufacturing process of ** porosity thin film which removes a solvent an application or after carrying out a spray, the solution of a viologen derivative Or the method of ** which the monomer and fusibility precursor of ** viologen de.ivative which produce a film after mixing the sol or the distributed solution of a gel are infiltrated into a solid-state macromolecule porosity thin film, or is made to react within hole an application or after carrying out a spray can be used.

[0016] In order to constitute ECD using the electrolyte thin film like the above, an electrolyte thin film is inserted by the transparent electric conduction electrode and the counter electrode. There are SnO2, ITO, etc. as a transparent electric conduction electrode, and a counter electrode can use the matter colorless by both electrode or oxidation-reduction reactions that carry out oxidization coloring, such as NiO, IrOx, and a Prussian blue, etc. If a viologen derivative receives electron from an ITO electrode, it will be returned and will color. At this time, since ITO will be returned if not much high voltage is impressed, less than [1V] is desirable.

[0017]

[Effect of the Invention] ECD of this invention is putting in the coloring matter into the electrolyte, and it is able to make it large in the area of for example, several 10cm angle for the cost to be cut down.

[0018]

[Example] An example is explained using a drawing. The example of EC display device is shown in drawing 1 . In this laminated structure, they are the lower shell glass plate 1, a counter elec.rode 2, the background board 3, the solid electrolyte film 4, the transparent electric conduction film 5, and a glass plate 6. Since this display device is reflective mode, a glass plate 1 does not necessarily need to be a transparent board, and a resin board etc. is sufficient as it. A counter electrode 2 has little generating of hydrogen or oxygen, and electronic conductivity material with large electric capacity with sufficient reversibility is used to an electrochemical oxidation-reduction reaction. Specifically, there is a composite of carbon, and transition metals and carbon etc. The thickness of a counter electrode 2 is about 0.1-10 micrometers.

[0019] The background board 3 has a common white background board, for example, the sheet

which kneaded and fabricated alumina powder with the binder can be used. The background board 3 can also be served by the counter electrode 2. The solid electrolyte film 4 sinks in the electrolytic solution which dissolved the trifluoromethane sulfonic-acid lithium supporting electrolyte and the viologen compound in the poly ethylene glycol monoether during hole of for example, a polyethylene porous membrane, and thickness is the solid electrolyte film which has the ion conductivity of 4-20 micrometers and 1.5 - 2.5x10-4 S/cm.

[0020] The transparent electric conduction film 5 is a collector, and it is the indium-tin-oxide (ITO) tin oxide etc., and thickness is 0.1-0.2 micrometers and is formed on a glass plate 6. The voltage impressed between the transparent electric conduction film 5 and a counter electrode 2 is about 0.5-1V. Since ITO will be returned if not much high voltage is impressed at this time, it is not desirable. In this way, since the electrolyte is fixed in the poly membrane, EC element created can be substantially dealt with as a solid-state film and there are no worries about a liquid spill even if structure is easy and it moreover assembles, and the handling at the time is also easy and damages after assembly, special cautions are unnecessary like [in the case of a liquid electrolyte].

[0021] By impressing negative voltage to the transparent electric conduction film 5 from a power supply, a viologen compound is returned and colored and a display is realized. Drawing 2 shows the example of a penetrated type modulated light element. The laminated structure is the order of a glass plate 11, the transparent electric conduction film 12, a counter electrode (display electrode) 13, the solid electrolyte film 14, the transparent electric conduction film 15, and a glass plate 16 from a lower layer.

[0022] With this structure, by using material of oxidization coloring nature, such as NiO, IrOx, a Prussian blue, and the poly aniline, for a counter electrode 13, and impressing voltage to it by making 15 into negative voltage among the transparent electric conduction films 12 and 15, the viologen compound of the electrolyte layer 14 has the special feature which can create high EC element of coloring efficiency in order to carry out reduction coloring. the point that the structure of drawing 2 differs from drawing 1 -- as a counter electrode 13 -- like **** -- IrOx etc. -- it uses, is formed by the thickness of 0.05-0.2 micrometers, and is the point which is light-transmission nature

[0023] With the structure of drawing 1 , the background board 3 may be light impermeability nature, and the light impermeability nature of a counter electrode 2 may also be permeability. With the structure of drawing 2 , it acts as modulated light glass (EC window) by impressing voltage by making the electric conduction film 15 into negative voltage between the electric conduction film 12 and 15. In addition, if a counter electrode 13 is patternized with this structure, it can be used also as a penetrated type display device.

[Translation done.]